Description

Method for generating an information item, support body in which the information item is generated, and use of such a support body

The invention relates to a method for generating an information item. It also relates to a support body in which the information item is generated and to a use of such a support body.

In order to obtain coloured information items, photochemical reactions are directly or indirectly part of daily life. Processes in the context of conventional silver halide photography include either wet-chemical operating steps, such as development and fixing in appropriate baths, or operations using organic dye systems, such as in the case of instant Polaroid pictures for example, which are nevertheless usually not light-fast.

In semiconductor development but also in the computer-aided creation of prototypes (rapid prototyping, rapid tooling), a large number of so-called photoresist materials or photo-prepolymers have become established on the market (Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2002 Electronic Release, Keyword Photoresists). In the widest sense, these are so-called prepolymers which polymerize, crosslink or cure as a result of photochemical reactions and stand out from the background as a separate information item written in the x,y-direction only in a subsequent step as a result of washing with solvents, as in the case of photolithography, or with a change in the z-coordinate, as in the case of rapid prototyping.

In order to achieve a relatively high spatial resolution and thus also a higher data and information density in

the abovementioned method, use is generally made of lasers. Conventional laser inscription methods are widely used in the production of identity cards, driving licences, bank cards, credit cards or the like which are made of plastic.

It is known from DE 29 07 004 C2 to apply visually readable information to identity cards by means of laser radiation. In this case, the information becomes visible by carbonization of the plastic material, wherein the information stands out in black or grey from a differently coloured background, e.g. opaque or transparent. It is not possible to produce other colours in this way. In this case, laser inscription is more secure against forgery or manipulation than other inscription methods because it can be carried out subsequently even in inner-lying layers.

Moreover, it is also known to engrave by means of laser radiation, in particular it is possible to locally remove individual layers of a multilayer card body. This is utilized in DE 30 48 733 C2 to apply differently coloured information items to identity cards. Here, use is made of a multilayer card body, the layers of which are differently coloured. By locally removing individual layers by means of laser radiation, the differently coloured layer located therebelow becomes visible. However, under some circumstances, this method of inscribing card-shaped data carriers has the disadvantage that the surface of the data carrier is damaged by the removal operation.

It is known from DE 44 17 343 A1 to form a single-coloured component and/or grey and black component of an image part in an identity card by means of laser technology and to apply a supplementary coloured image part on top of this in a congruent manner with respect to the image, in particular using the heat transfer method.

In the latter method, point electrodes of a row of thermal printers are heated in an electrically controlled manner so that the colour layer of a coloured film or multicoloured film introduced between the row of thermal printers and the top layer is melted and/or evaporated at points and deposited on the top layer. The varied processing of the card with highly technical devices produces a high depth of colour which makes it more difficult to forge using widely available colour copiers and colour printing techniques, but requires a method which is complicated in terms of apparatus.

DE 199 55 383 A1 describes a method for applying coloured information items to an object by means of laser radiation of at least two different wavelengths, wherein the colour of the layer can be set by wavelength-selective fading of individual organic pigments as a result of subtractive colour mixing.

DE 100 11 486 A1 also describes a card-shaped data carrier and a method for producing the same, which makes it possible to apply coloured information items by means of laser processing without damaging the surface of the data carrier. In this case, a layer is completely faded locally by the laser radiation so that the layer is at least virtually transparent per se in the laser inscription spot. In this way, a spot which was originally black, grey or dark brown can be set to be red, blue or green, depending on which of the laser-sensitive layers in the sandwich structure are faded.

It is an object of the invention to provide a method for generating an information item in and/or on a support body, which, using simple means, has a particularly high long-term resistance, in particular to light and moisture. A support body which is particularly suitable for this method is also to be provided, and also a use of such a support body is to be specified.

With regard to the method, this object is achieved according to the invention in that, for a number of starting materials contained in and/or on the support body, those reaction conditions which cause the starting materials to enter into a synthesis reaction are set in a localized partial area of the support body by means of laser irradiation.

The invention is based on the consideration that, in systems known to date, the long-term stability of the information item is limited inter alia by the fact that colour conversion reactions continue in an uncontrolled manner even without targeted and desired activation, e.g. by means of irradiated sunlight. This activation may be effected by statistical stimulations of a conventionally used dissociation reaction since, in a dissociation reaction in which just one starting material is required, the reaction conditions required to break down the molecule into simpler molecules, atoms, ions or radicals can be achieved in a relatively simple manner. For example, fading may occur as a result of photochemical decomposition, and this may lead to the destruction both of the information item and of the support body. The concept of generating a long-term-resistant information item is therefore a deviation from such simple decolouring processes. An increase in the long-term stability of the information item is to be achieved in such a way that the probability of subsequent, statistically triggered conversion processes is consequently reduced. This can be achieved by a targeted increase in the complexity of the conversion reaction employed, with accordingly higher reaction conditions which are more difficult to achieve. For an accordingly increased complexity of the reaction processes, therefore, use is made of types of reaction which are based on the use of a plurality of starting materials or other complex reaction parameters. The generation of an

information item which is resistant to light and moisture is achieved by synthetic processes instead of destructive processes or dissociation.

Such synthesis reactions preferably include additions, eliminations, substitutions and in particular redox and complexing reactions. In addition reactions, atoms or groups of atoms are added to a multiple bond. In elimination reactions, contrary to addition reactions, atoms or groups of atoms are removed from a molecule without others being added in their place. Substitution is characterized by the replacement of an atom or group of atoms in a molecule by other atoms or groups of atoms, wherein a covalent bond with one partner is broken and then another is formed with another partner. The redox reaction is characterized by electrons being discharged by one partner (reducing agent) and taken up by the other partner (oxidizing agent). In complexing reactions, a central atom or ion is surrounded by a number of other atoms, ions or molecules, the so-called ligands, in a spatially uniform arrangement.

With these synthetic processes, demanding or complex requirements are placed on the reaction conditions and reactands.

As reaction conditions, a sufficiently high reaction temperature, a release of reactive starting materials or activated molecule species in a number sufficient for the reaction and/or a sufficiently high particle mobility of the reaction partners are particularly important. These reaction conditions can be achieved by introducing thermal energy in a spatially resolved manner by means of laser light, said thermal energy providing the activation energy of the process. By virtue of the thermal energy, the mobility of the starting materials in or on the support body is improved and thus the probability of reaction is increased to such an extent that a sufficient

reaction yield is achieved. Moreover, irradiation with laser light makes it possible for reaction-inhibiting surroundings to be broken up and thus for the starting materials to be made available at all as reactands.

Without energy being supplied, the starting materials contained in the support body would not be induced to result in a property or substance change so as to generate a durable information item. Their statistical probability of reaction would therefore be lowered for example in comparison with the reaction partners of a fading process. For this reason, under normal ambient conditions, it would neither be possible to achieve the activation energy required to produce reactive molecule species from the starting materials nor to have available the reactive molecule species under normal conditions in a sufficient local concentration to initiate a reaction or even achieve a complete reaction conversion. Another condition for suitable starting materials is inertia with respect to the support body itself, so that the latter is not durably changed by the starting materials and thereby possibly damaged or made unusable. As starting materials contained in the support body, consideration may therefore be given in principle to substance mixtures or compounds of all the elements of the Periodic Table which are suitable for such a "robust" use. In particular, these criteria are preferably met by selected inorganic substance mixtures since these migrate to a relatively small extent in the support body and enter into reactions resulting in a substance or property change usually only at high temperatures of several hundred degrees Celsius, such as inside a Bunsen burner flame for example.

In order to detect the property or substance change of the starting materials which is caused by laser irradiation, use is advantageously made of the change in their absorption properties with regard to the wavelengths in the ultraviolet to infrared range. For

particularly simple detection, the starting materials are preferably selected in such a way that they are caused to enter into a synthesis reaction resulting in a change in colour. A coloured information item is thus preferably produced.

For one or more coloured information items selected as required, the starting materials of the synthesis reactions resulting in different colour changes are preferably selected in such a way that the product of the respective synthesis reaction is in each case assigned to a basic colour of a CMYK colour scale for Cyan, Magenta, Yellow and Key or blacK. Single or mixed colours can thus be generated given a suitable combination.

In order to allow a graphically wide-ranging assortment of coloured patterns and variations in the support body, the starting materials of synthesis reactions resulting in different colour changes are preferably contained in the support body in separate volume segments.

In order to produce differently coloured information items and information items in a support body with a relatively high depth of colour, in particular including with regard to laser inscription which is particularly secure against forgery and manipulations, an internal coloured design is also advantageous in addition to the external coloured design of support bodies. The starting materials assigned to different colour reactions are therefore preferably contained in the support body in separate layers.

In order to prevent premature reaction of the starting materials without stimulation by means of laser irradiation, a protective device or measure which suppresses this reaction is advantageously provided. For this reason, preferably at least one of the starting materials is contained in the support body in an

encapsulated manner, wherein the encapsulation is advantageously selected in such a way that it is broken open by the laser radiation and releases the relevant starting material as a reaction partner. To this end, the encapsulation is preferably configured in such a way that it absorbs the laser radiation itself. The generation of an information item in a temporally and spatially targeted manner is thus ensured.

Preferably, auxiliary agents or layers which absorb the laser radiation are embedded in the support body in order to focus the laser radiation in a targeted manner directly onto at least one starting material, particularly if the latter alone is not suitable or is not sufficiently suitable for absorbing the laser radiation, or in order to reduce the necessary laser energy. One example of an absorbent auxiliary agent which may be used is a mica pigment which is commercially available under the name "Iriodin" or "Mica". As a result, the laser light irradiated onto the auxiliary agent is transferred to the selected starting material by interference or reflection effects. This leads at this point to a local increase in temperature, a so-called hot spot, and thus to stimulation of at least one starting material with usually at least one further starting material, so that these starting materials interact and enter into a synthesis reaction.

In order to reduce the activation energy of the reaction partners, particles which act as a catalyst are preferably embedded in the support body. As a result it is possible, depending on the selected starting materials, to use a relatively low laser energy or even a relatively low-power laser. The catalytic elements may in particular come from the 8th subgroup, the so-called platinum metals. Finely disperse platinum, rhodium, palladium or mixtures thereof may catalyse redox reactions in particular, in a manner analogous to their

use in exhaust gas catalysts. A decomposition of a platinum complex, such as for example a decomplexing of the orange-red $(CH_3)_3PtI$, would also be conceivable. By virtue of a decomposition of $(CH_3)_3PtI$, on the one hand elemental platinum can be obtained as catalyst or, at a relatively high concentration, even a blackening as a result of finely disperse platinum can be produced.

In order to generate an information item in a support body in a particularly simple manner with a low complexity in terms of apparatus and technique and for a high spatial resolution, and thus also to achieve a relatively high data and information density, preferably all commercially available lasers with emissions from the UV to IR range can be used to inscribe documents, e.g. with emissions of 190 nm for photolithography or with emissions of 10 μm for inscribing packaging by means of a CO_2 laser. In one particularly advantageous inscription embodiment, use is made of an Nd:YAG laser with an emission of 1064 nm.

In one particularly advantageous embodiment of the method, substances which do not absorb the laser radiation, such as paper, plastic films and/or a layer of colour, adhesive and/or varnish, are preferably provided as basic components of the support body, these substances advantageously being inscribed or marked so as to mark documents in a forgery-proof manner or to verify documents by machine and at the same time make them invalid.

In one particularly advantageous embodiment of the method, the starting materials contained in and/or on the support body are preferably introduced as an additional additive during film production methods, such as calendering, extrusion or film casting, or into the paper pulp during paper manufacture and/or are advantageously applied in and/or on the support body by means of coating

methods, such as painting, misting, spraying, coating or dipping, and/or by means of printing methods, such as offset printing, die stamping, photogravure, flexographic printing, screen printing, indirect letterpress printing, heat transfer printing, electrophotography and inkjet methods.

With regard to the support body, the aforementioned object is achieved in that a number of starting materials are contained in and/or on said support body in such a way that the reaction conditions for a synthesis reaction of the starting materials can be set in a laser-induced manner.

Substances which do not absorb the laser radiation, such as paper, films, particularly thermoplastic plastics, and/or a layer of colour, adhesive and/or varnish, are preferably provided as basic components of the support body.

In order to detect the property or substance change of the starting materials which is brought about by the laser radiation, use may advantageously be made of the change in their absorption properties with regard to wavelengths from the ultraviolet range, through the visible range and up to the infrared range. For particularly simple detection, the starting materials are advantageously selected in such a way that they are caused to enter into a synthesis reaction resulting in a change in their colour which is visible to the human eye. For synthesis reactions resulting in colour reactions, inorganic substance mixtures are advantageously used as the starting materials. By virtue of such starting materials, intensive coloured information items can be generated in particular by way of redox or complexing reactions, said information items being particularly resistant to light and moisture, etc. and thus also being suitable for marking documents of value and/or security

documents with a particularly high level of security against forgery. Words and images, such as inscriptions, logos or barcodes, can in particular be generated as the coloured information items.

For one or more single-coloured or multicoloured information items selected as required, the starting materials in the support body are preferably selected in such a way that the product of the respective synthesis reaction is in each case assigned to a basic colour of a CMYK colour scale for Cyan, Magenta, Yellow and Key or blacK.

In order to be able to use the support body in a particularly varied manner, the support body is advantageously equipped for the generation of permanent, intensive coloured information items. $MnSO_4$, KNO_3 and KOH are preferably contained as the starting materials for a product assigned to the colour blue ("Cyan"). Alternatively or cumulatively, $Fe_2(SO_4)_3$ and KSCN are preferably contained as the starting materials for a product assigned to the colour red ("Magenta"). Alternatively or cumulatively with the colours blue ("Cyan") and/or red ("Magenta"), Cr_2O_3, KNO_3 and KOH are preferably contained as the starting materials for a product assigned to the colour yellow ("Yellow").

In order to increase the variety of coloured information items, Cu^{2+} and NH_3 for the reaction to form the tetrammine-copper complex or the substances $Co(NO_3)_2$ and Al_2O_3 are preferably contained as the starting materials for a product assigned to the colour blue and/or $Co(NO_3)_2$ and ZnO or the substances K_2CrO_4 and C_3H_7OH are preferably contained as the starting materials for a product assigned to the colour green.

In order to allow a graphically wide-ranging assortment of coloured patterns and variations in the support body,

the starting materials of synthesis reactions resulting in different colour changes are preferably contained in the support body in separate volume segments.

In order to produce differently coloured information items in a support body with a relatively high depth of colour, in particular including with regard to laser inscription which is particularly secure against forgery and manipulations, an internal coloured design is also advantageous in addition to the external coloured design of support bodies. The starting materials assigned to different colour reactions are therefore preferably contained in the support body in separate layers.

In order to focus the laser radiation directly onto at least one starting material, particularly when the latter alone is not suitable or is not sufficiently suitable for absorbing the laser radiation, without destroying the support body with too high a laser energy, auxiliary agents or layers which absorb the laser radiation are preferably embedded in the support body.

In one particularly advantageous embodiment of the support body, a mica pigment such as "Iriodin" or else simply titanium dioxide or carbon in the form of carbon black or advantageously also a colour pigment such as phthalocyanine, is preferably contained in said support body, assigned to Key or blacK, alternatively or cumulatively with the colours blue ("Cyan"), red ("Magenta") and/or yellow ("Yellow"), as an auxiliary agent which transfers the irradiated laser radiation to a selected starting material via interference or reflection effects.

In order to be able to use the support body in a reliable and flexible manner in terms of time and location, the starting materials provided therein for a synthesis reaction are preferably at least partially surrounded by

an encapsulation which inhibits this reaction until it is stimulated by laser radiation. With particular advantage, the encapsulation is selected in such a way that it is broken open by the laser radiation and releases the relevant starting material as a reaction partner only when said encapsulation is broken up. To this end, the encapsulation is preferably configured in such a way that it absorbs the laser radiation itself.

In order to reduce the activation energy, particularly for redox reactions of the starting materials contained in the support body, and to promote the use of a relatively low-power laser, particles which act as a catalyst are preferably embedded in the support body.

The support body equipped in this way can advantageously be used in all fields involving documents of value and/or security documents, in the logistics sector or ticketing and for presentations. The support body is therefore preferably used as an identification card, driving licence, credit card, health insurance card, ticket or foil.

The advantages which can be achieved by virtue of the invention are in particular that resistant information items can be generated by the synthesis reaction of a number of starting materials. Typical and sensitive detection reactions for subgroup metals, as known in particular from the literature, can be used to generate particularly intensive coloured information items which are resistant to environmental influences. Simply by irradiating at least one reactand with laser light, it is possible to carry out the method in a reliable manner. The laser irradiation ensures that a reaction temperature which is just high enough for the desired synthesis reaction is provided and/or that the irradiated substances are moved to a sufficiently great extent and/or are caused to release reactive molecule species.

Furthermore, by virtue of the fact that it is particularly suitably equipped with encapsulations of particularly reactive starting materials, with the auxiliary agents or layers which absorb the laser radiation and/or with catalytically active particles, the support body makes it possible for the method to be carried out in a targeted and controlled manner. For example, if the starting materials of a synthesis reaction are reactive with one another at room temperature or by rubbing, at least one of the starting materials is contained in the support body in an encapsulated manner, in order that the synthesis reaction is made possible only when the encapsulation is broken open in a laser-induced manner. On the other hand, a starting material which does not absorb the laser radiation or which absorbs it only slightly is activated by the laser radiation indirectly via auxiliary agents or layers which absorb the laser radiation and are embedded in the support body, in that the laser radiation is focussed onto the selected starting material via interference or reflection effects of the auxiliary agents or layers, and thus a hot spot is produced there on account of the local increase in temperature, at which hot spot the starting material is made to interact with at least one other starting material or is brought to a monomolecular reaction. Catalytically active particles embedded in the support body reduce the activation energy of the starting materials.

Moreover, by embedding the starting materials of synthesis reactions resulting in different colour changes in separate volume segments and/or layers, the support body allows a high flexibility for desired graphic designs in the form of many colour variations and colour patterns. The method for the laser-induced in-situ generation of information items in the support body thus permits a use for the marking or inscription of papers,

films and other plastic documents, increases in particular the security against forgery of a document marked in this way, and can furthermore be used to verify documents by machine and at the same time make them invalid, such as tickets for example. The method can thus be used in all sectors of daily life which involve the rapid and spatially targeted application and/or incorporation of durable words and/or images, etc.

An example of embodiment of the invention will be described in more detail below.

In the text which follows, a description will be given of various starting materials, their incorporation in and/or on a support body and also the laser initialization thereof, which permits a wavelength-specific effect over the UV-VIS-IR range.

Depending on the application, the starting materials selected for a desired synthesis reaction may be introduced by means of diverse incorporation or application methods into an inner and/or outer region of a data carrier acting as support body, in a spatially precise manner and in the form of a matrix or layer. As basic components or composite materials on which the support body is based, use may be made for example of paper or plastic films and also of layers of colour, adhesive or varnish applied therebetween and/or thereon. In one preferred embodiment, the starting materials are introduced as an additional additive during manufacture of the film. This relates in particular to customary film manufacturing methods, such as calendering, extrusion and film casting. The starting materials selected for the synthesis reaction can also be incorporated as an additional additive into the paper pulp during paper manufacture. Incorporation into films and papers has the advantage that no significant interventions are required in the production process itself during the production of

documents, such as cards and identification documents for example. The starting materials selected for a desired synthesis reaction can be introduced into and/or onto the support body by means of various coating methods, such as painting, misting, spraying, coating or dipping, and/or by means of printing methods, such as offset printing, die stamping, photogravure, flexographic printing, screen printing, indirect letterpress printing, heat transfer printing, electrophotography and inkjet methods.

In one preferred embodiment, a screen printing varnish which is highly charged with the starting materials is printed onto an opaque plastic film and laminated over with a number of layers of plastic film. This procedure represents a particularly flexible embodiment since it can be used to achieve internal prints during the production of composite materials, such as cards and identification documents made fully of plastic or of paper/plastic compounds.

Of course, besides the complexing and redox reactions of the starting materials contained in the support body, as mentioned in the example of embodiment below, other synthesis reactions are also conceivable, such as eliminations for example, in which part of the molecule is cleaved, whereby its physical properties also change, or additions, in which new covalent bonds are formed and thus a "new" substance is generated, or substitution reactions, in which ligands of a complex are replaced for example.

Example 1: Blue laser inscription

A stoichiometric mixture of the inorganic starting materials consisting of cobalt(II) nitrate with aluminium sulphate and a binder is printed onto a plastic card, for example by screen printing. The mixture optionally also contains "Iriodin" (< 0.5 percent by weight). This plastic card can then be laminated over with an NIR-

transparent overlay film. During irradiation with an Nd:YAG laser, the reaction to form the cobalt spinel $CoAl_2O_3$, known in the literature as Thenard's Blue, is brought about at the hot spot generated by the laser. In the expanded recipe, the "Iriodin" serves as an auxiliary agent which absorbs the laser radiation, in order to transfer the laser radiation to the starting materials and thus to focus it onto the starting materials and/or to minimize the laser energy required for the reaction. This is because laser radiation which is too strong usually leads to carbonization, which may minimize or cover over the blue colour effect.

The reaction to form Thenard's Blue can be described by the following equation:

$Co(NO_3)_2 + Al_2O_3 \rightarrow CoAl_2O_3 + 2\ NO_2 + \frac{1}{2}\ O_2$

Fig. 1 schematically shows a pigment 2, "Iriodin", which is embedded in a matrix 1 and absorbs the irradiated laser light 6 in its mica core 4 and transfers it, as shown by a lightening flash 8 in Fig. 1, via interference effects, to the inorganic starting materials $Co(NO_3)_2$ and Al_2O_3 which are located at its boundary 10 in the matrix 1. A hot spot 12 is thus produced at the boundary 10 of the pigment 2, so that the reaction described in Example 1 is initiated, resulting in a change in colour.

Example 2: Green laser inscription

A stoichiometric mixture of the inorganic starting materials consisting of 2 cobalt(II) nitrate with 1 zinc oxide is added as an additive during film production in the example of embodiment, e.g. in the calendering process. The mixture optionally also contains a quantity of "Iriodin" (< 0.5 percent by weight). In the example of embodiment, this film is then combined with other components to form a plastic card which is covered only with an NIR-transparent overlay film. During irradiation with an Nd:YAG laser, the reaction to form the zinc

cobalt spinel $ZnCo_2O_4$, known in the literature as Rinmann's Green, is brought about at the hot spot generated by the laser. In the expanded recipe, the "Iriodin" once again serves as an auxiliary agent which absorbs the laser radiation, in order to focus the laser radiation onto the starting materials and/or to minimize the laser energy required for the reaction. This is because laser radiation which is too strong usually leads to carbonization, which may minimize or cover over the green colour effect.

The reaction to form Rinmann's Green can be described by the following equation:

$2\ Co(NO_3)_2 + ZnO \rightarrow ZnCo_2O_4 + 4\ NO_2 + ½\ O_2$

Example 3: Blue ("Cyan") laser inscription

A stoichiometric mixture of the inorganic starting materials consisting of pink-coloured manganese(II) sulphate with 2 potassium nitrate and 2 potassium hydroxide is added as an additive to an adhesive during hot-melt film production in the example of embodiment. The mixture optionally also contains a quantity of "Iriodin" (< 0.5 percent by weight). In the example of embodiment, this film is then combined with other components to form a plastic card which is covered only with an NIR-transparent overlay film. During irradiation with an Nd:YAG laser, the reaction to form green-blue ("Cyan") manganate, also known as an oxidation melt, is brought about at the hot spot generated by the laser. In the expanded recipe, the "Iriodin" once again serves as an auxiliary agent which absorbs the laser radiation, in order to focus the laser radiation onto the starting materials and/or to minimize the laser energy required for the reaction. This is because laser radiation which is too strong usually leads to carbonization, which may minimize or cover over the green-blue ("Cyan") colour effect.

The reaction to form green-blue ("Cyan") manganate can be described by the following equation:
$MnSO_4 + 2\ KNO_3 + 2\ KOH \rightarrow K_2MnO_4 + 2\ KNO_2 + H_2SO_4$

<u>Example 4: a) Yellow ("Yellow") laser inscription and b) green laser inscription</u>

a) A stoichiometric mixture of the inorganic starting materials consisting of green chromium(III) oxide with 3 potassium nitrate and 2 potassium hydroxide is incorporated in a matrix in a manner analogous to one of Examples 1 to 3. There is no need to use "Iriodin" in this example of embodiment since Cr^{3+} absorbs very well in the red spectral range. During irradiation with a high-power dye laser or semiconductor laser with red emission (630 - 690 nm), the reaction to form yellow-orange ("Yellow") dichromate (Cr^{6+}), also known as the chromium oxidation melt, is brought about at the hot spot generated by the laser.

The redox reaction to form yellow-orange ("Yellow") dichromate can be described by the following equation:
$Cr_2O_3 + 3\ KNO_3 + 2\ KOH \rightarrow K_2Cr_2O_7 + 3\ KNO_2 + H_2O$

b) As a colour reaction from yellow to green, use may be made of the reaction, also known as the "conventional alcohol test" in test-tubes, of yellow potassium chromate (Cr^{6+}) with propanol, which is present at least in trace amounts in many printing additives, to form green chromium(III) oxide according to the equation:
$2\ K_2CrO_4 + 3\ C_3H_7OH \rightarrow Cr_2O_3 + 3\ C_3H_6O + 4\ KOH + H_2O$
When implemented in a support body, the mobility of the system must be minimized for example by lamination, in order to prevent health risks which may arise on account of the poisonous chromates.

Fig. 2 schematically shows a pigment 2, yellow chromate (Cr^{6+}), which is embedded in a matrix 1, wherein the matrix 1 contains traces of an alcohol (R-OH) as reducing

agent 14. The lightening flash 8 symbolizes a hot spot 12 induced by the irradiated laser light 6 at the boundary 10 of the pigment 2 (Cr^{6+}) to the matrix 1. At that location, the alcohol is oxidized to form an aldehyde (R-HO) and the Cr^{6+} reduces to form green Cr^{3+}, according to the equation described in Example 4b).

Example 5: Red ("Magenta") laser inscription

a) Iron in the oxidation stage +3, e.g. iron(III) sulphate, forms with thiocyanates, even in non-aqueous medium, a deep-red ("Magenta") characteristic complex according to the equation:

$Fe_2(SO_4)_3 + 6\ KSCN\ (+\ 6\ H_2O) \rightarrow 2\ [Fe(SCN)_3(H_2O)_3] + 3\ K_2SO_4$

The complex forms as soon as the starting materials rub against one another, and therefore the iron(III) sulphate is incorporated in the matrix in encapsulated form and the laser radiation breaks open the encapsulation to initiate the reaction, resulting in a change in colour.

b) Iron(II) sulphate does not require any encapsulation. With potassium nitrate and potassium thiocyanate and water, the action of a laser oxidizes it to form iron with the oxidation stage +3, which immediately reacts to form the deep-red ("Magenta") characteristic complex according to the equation:

$$2\ FeSO_4 + KNO_3 + 6\ KSCN + 4\ H_2O \rightarrow 2\ [Fe(SCN)_3(H_2O)_3] + KNO_2 + 2\ K_2SO_4 + 2\ KOH$$

Example 6: Red fluorescent laser inscription

Europium with the oxidation stage +2, upon oxidation with nitre to oxidation stage +3 following laser irradiation, in a blue fluorescent environment exhibits a spatially limited red fluorescence.

The redox reaction can be described by the following equation:

$$2\ Eu^{2+} + KNO_3 + H_2O \rightarrow 2\ Eu^{3+} + KNO_2 + 2\ OH^-$$

Example 7: Multicoloured laser inscription

The starting materials presented in Examples 3, 4 and 5 for their laser-induced characteristic colour reactions may likewise be embedded, combined with one another, in different, separate layers 16a-d which respectively form a support body with an appropriate reactive matrix, as shown in **Fig. 3**. In the example of embodiment, a film composite structure comprising four differently doped layers 16a-d is provided, wherein the lowermost layer 16a is doped with $MnSO_4$, KNO_3 and KOH (Example 3), the second-lowest layer 16b is doped with $Fe_2(SO_4)_3$ and KSCN (Example 5), the third layer 16c from the bottom is doped with Cr_2O_3, KNO_3 and KOH (Example 4) and the uppermost layer 16d is doped with "Iriodin". The respective synthesis reaction is initiated by irradiation with an Nd:YAG laser. To this end, the laser is focussed, for example through confocal optics, onto selected volume segments 18a-d within the respective layer 16a-d (z-coordinate) at certain positions (x,y-coordinates). Resolutions of around 10 μm in the x,y-direction and of around 30 μm in the z-direction are achieved. On account of the relatively low focussing sharpness in the z direction, each layer 16a-d is individually gridded in order to carry out the synthesis reaction on the selected volume segments 18a-d. In the example of embodiment, a colour change to blue ("Cyan") is achieved in the lowermost layer 16a by the reaction of $MnSO_4$ with KNO_3 and KOH (Example 3). In the second step, the laser is then adjusted onto the second-lowest layer 16b and focussed onto the desired x,y positions within the latter. As a result of the irradiation, a colour change to red ("Magenta") is brought about here by virtue of the reaction of $Fe_2(SO_4)_3$ with KSCN (Example 5). In an analogous manner, in the third layer 16c from the bottom, the reaction of Cr_2O_3, KNO_3 and KOH is induced in the selected volume segment 18c and thus the colour change to yellow ("Yellow") is achieved (Example 4). Finally, in the example of embodiment, spatially resolved irradiation

is carried out in the uppermost layer 16d which is doped with "Iriodin". By virtue of the local overheating in the selected volume segment 18d, a grey to black colour change is brought about which represents the Key. If the film composite structure is viewed perpendicular to the layers 16a-d following the laser-induced inscription process, a fully coloured CMYK image is produced as a result of subtractive colour mixing by virtue of the superposition of the individually coloured volume segments 18a-d. By virtue of the aforementioned spatial resolutions, images having a resolution of more than 600 dpi are possible, which thus corresponds to the standard resolution of modern colour printers.

List of references

1	matrix
2	pigment
4	mica core
6	irradiated laser light
8	lightening flash
10	boundary
12	hot spot
14	reducing agent
16a-d	layer
18a-d	volume segment